

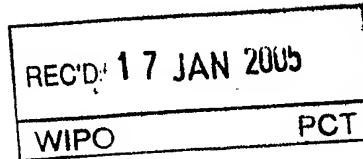


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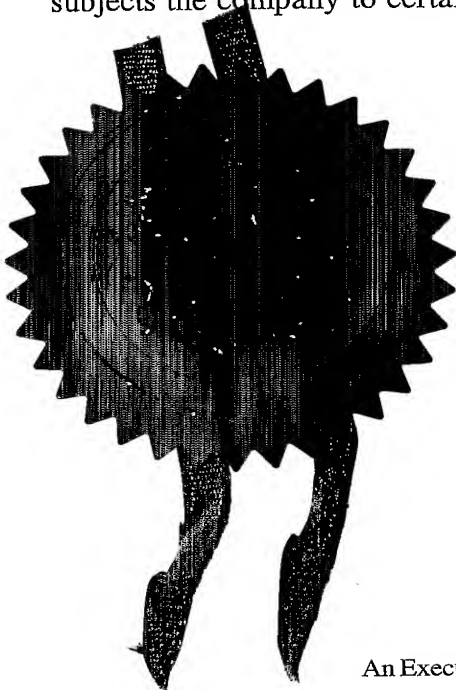


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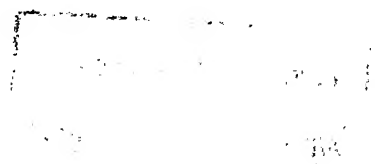
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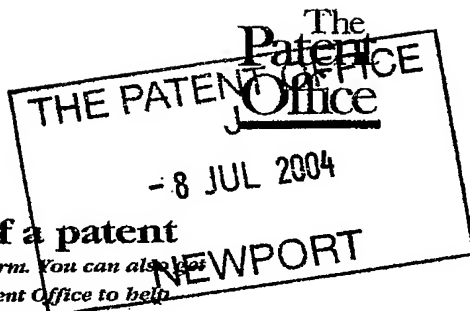
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09/77

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1. Your reference

SMC 60665/GB/P1

08JUL04 E909732-1 D02944

P01/7700 0.00 0415310.2 NONE

2. Patent application number

(The Patent Office will fill in this part)

0415310.2

- 8 JUL 2004

3. Full name, address and postcode of the or of each applicant (underline all surnames)

Avecia BV
Sluisweg 12
PO Box 123
5140 AC Waalwijk

Patents ADP number (if you know it)

7784002001

If the applicant is a corporate body, give the country/state of its incorporation

The Netherlands

4. Title of the invention

COATING COMPOSITIONS

5. Name of your agent (if you have one)

SCHMITT, Maja

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Avecia Limited
PO Box 42, Hexagon House
Blackley
Manchester, M9 8ZS

Patents ADP number (if you know it)

7742125001

7764137001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number
(if you know it)

Date of filing
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
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Patents Form 1/77

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Description

22

Claim(s)

03

Abstract

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Statement of inventorship and right to grant of a patent (*Patents Form 7/77*)

Request for preliminary examination and search (*Patents Form 9/77*)

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11. I/We request the grant of a patent on the basis of this application.

Signature

G. Shepherd

Date

7/7/04

Avecia Limited Authorised Signatory

12. Name and daytime telephone number of person to contact in the United Kingdom

Mrs K.M. Pinder/Mrs G. Shepherd 0161 721 1361/2

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COATING COMPOSITIONS

The invention relates to aqueous urethane-vinyl combination polymers suitable for coating compositions, processes for the manufacture of such compositions and coatings derived therefrom which exhibit a high level of stain resistance.

5 Stain resistance is a key property required by the coatings industry for a surface coating on porous substrates such as on wood. In particular this includes resistances towards ethanol, coffee, red wine and mustard.

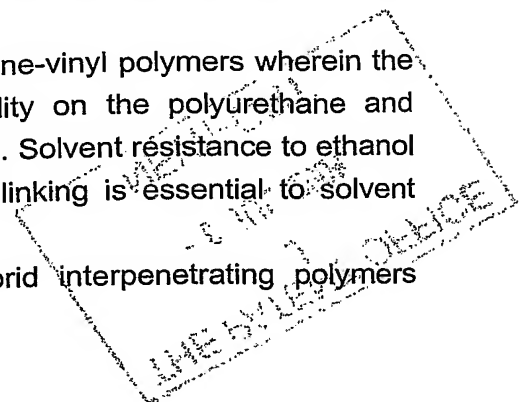
10 Current coating products are predominantly based on crosslinked solvent borne polymers, which are undesirable because of unacceptably high volatile organic content (VOC) emissions. The use of waterborne polymers reduces VOC emissions, but substantial crosslinking of the polymer is necessary for adequate stain resistance. External crosslinking agents incur problems because of both toxicity during handling and in uniform mixing with the polymer dispersion. Internal crosslinking, achieved by incorporation of appropriate functionalities into the polymer chain, has limitations with respect to the overall accessibility of the crosslinking functionalities and the point in the film forming process when crosslinking occurs. Consequences of this are films with inferior sensitivity to stains and the formation of less compact or permeable films with poor barrier properties.

20 It is well known in the coating industry that polyurethane coatings exhibit excellent mechanical properties together with useful resistances to chemicals and solvents. Conventional urethanes for coatings are prepared in organic solvents and subsequently crosslinked to provide useful coatings. A drawback of these coatings is the high VOC emissions, which has been addressed by the use of water dispersible polyurethanes. It is now also known that the properties of coatings can be modified and improved by incorporation of vinyl polymers, and in particular acrylic polymers, into the dispersions. This may be effected either by means of a simple blend of the preformed polyurethane and vinyl dispersions or by polymerisation *in situ* of the vinyl component in the presence of the preformed polyurethane to form a hybrid system. The hybrid process is described fully in US 5173526.

30 US 6063861 describes self-crosslinkable polyurethane-polyacrylate hybrid dispersions formed by polymerisation of an acetoacetoxy-containing vinyl monomer in the presence of a polyurethane, and further containing a difunctional amine. Solvent resistances to water, ethanol and acetone were reported.

35 US 5977215 describes self-crosslinkable polyurethane-vinyl polymers wherein the crosslinking is provided by pendant carboxyl functionality on the polyurethane and pendant epoxide groups provided by glycidyl (meth)acrylate. Solvent resistance to ethanol determined by swell-ratio measurement shows that crosslinking is essential to solvent resistance.

US 6239209 describes polyurethane-acrylic hybrid interpenetrating polymers



comprising air curable ethylenic unsaturated functionality which give rise to films of good chemical resistance to water, coffee, tea and mustard.

US 6342558 describes a polyurethane-polyacrylate hybrid which comprises an external crosslinking component which is reactive with at least one of the polyurethane and the polyacrylate, and wherein the polyurethane has a glass transition temperature of $\leq 0^{\circ}\text{C}$. Films from the compositions have improved chip resistance. No solvent resistance or chemical resistance properties are inherent.

EP 0742239 describes a composition comprising crosslinkable hydroxy-containing hybrid polymers and a water-dispersible polyisocyanate crosslinker wherein the hybrid polymers comprise a water-borne hydroxy-terminated polyurethane prepolymer/acrylate, preferably a hydroxy-acrylate. High crosslink density is described as necessary for good solvent resistance.

EP 0643734 describes a urethane-acrylic combination, where the urethane comprises at least one polyester polyol which incorporates polymerised units derived from a dimer acid, which is necessary to obtain solvent resistance of the polymer in a clear coating. No specific description of the type of acrylic is taught.

WO99/16805 describes a urethane-vinyl composition where the urethane polymer component has an acid value of ≥ 44 mg KOH/g of prepolymer solids. No specific description of the vinyl backbone is taught. Spot tests for water, and coffee and detergent resistance are reported.

We have now surprisingly found that careful selection of a combination of urethane and vinyl polymer components to give a urethane-vinyl hybrid can offer unexpectedly good stain resistances.

According to the present invention there is provided an aqueous coating composition comprising:

(i) 20 to 80 wt% of a polyurethane A which has an acid value between from 8 to 40 mg KOH/g polyurethane A and a hard segment content of $\geq 40\text{wt}\%$ by weight of polyurethane A; and

(ii) 20 to 80 wt% of a vinyl polymer B which has a glass transition temperature of $\geq 20^{\circ}\text{C}$;

wherein (i) and (ii) add up to 100 %;

which when in the form of a film exhibits a moisture vapour transmission rate of $\leq 500\text{g/m}^2/24\text{h}$.

For the purposes of the invention an "aqueous coating composition" means a dispersion or composition of a polymer in a liquid carrier medium of which water is the principle or only component; that is, water comprises at least 50% of the liquid carrier medium which may further comprise one or more organic solvents or diluents. Such a composition will typically comprise colloidally dispersed polymer particles, i.e. will typically be in the form of an aqueous polymer latex.

It is evident from all the foregoing that the term "polyurethane" as used in this

specification can mean one or more than one polyurethane, and is intended to apply not only to polymers (or prepolymers) having only urethane linkages formed from isocyanate and hydroxyl groups, but also to polymers, prepolymers or polymer segments having, in addition to urethane linkages, linkages formed from isocyanate groups and groups such as primary or secondary amines or thiols.

Preferably in the composition of the present invention polyurethane A is obtained by the reaction of:

(a) an isocyanate-terminated prepolymer formed from components which comprise:

(1) 20 to 80 wt% of at least one polyisocyanate;

(2) 3 to 10 wt% of at least one polyol of weight average molecular weight less than 500 Daltons, containing at least one ionic or potentially ionic water-dispersing group, and having at least one isocyanate-reactive group;

(3) 0 to 15 wt% of at least one polyol containing non-ionic water dispersing groups having at least one isocyanate-reactive group;

(4) 30 to 80 wt% of at least one polyol other than (2) or (3), having at least one isocyanate-reactive group;

where (1), (2), (3), and (4) add up to 100%; and

(b) an active-hydrogen chain extending compound.

For the purposes of the present invention, the hard segment content of a polyurethane is defined as the sum of the wt% of:

(i) polyisocyanate containing components (a)(1);

(ii) active hydrogen chain extending material (b) of molecular weight \leq 200 Daltons;

(iii) all polyol components (a)(2)

(iv) ring structure present in polyol components (a)(3) and (a)(4).

Ring structures (iv) may be part of aliphatic diol components such as for example cyclohexanedimethanol and cyclohexanediacid, or part of aromatic diol components such as for example bis-phenol-A and isophthalic acid.

Polyurethane A may also comprise olefinic functionality, for example through the incorporation of HEMA (2-hydroxyethylmethacrylate) into the polyurethane.

The organic polyisocyanate (1) used for making the prepolymer of the polyurethane A is preferably an aliphatic (which term includes cycloaliphatic), araliphatic or aromatic polyisocyanate, or a mixture of aliphatic and aromatic polyisocyanates, and is preferably a diisocyanate.

Examples of suitable aliphatic polyisocyanates include ethylene diisocyanate, 1,6-hexamethylene diisocyanate, isophorone diisocyanate, cyclohexane-1,4-diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, cyclopentylene diisocyanate, p-tetramethylxylene diisocyanate (p-TMXDI) and its meta isomer (m-TMXDI), hydrogenated 2,4-toluene diisocyanate, hydrogenated 2,6-toluene diisocyanate, and 1-isocyanato-1-methyl-3(4)-isocyanatomethyl-cyclohexane (IMCI).

Suitable non-aliphatic polyisocyanates include p-xylylene diisocyanate, 2,4-toluene

diisocyanate, 1-4-phenylene diisocyanate, 2,6-toluene diisocyanate, 4,4'-diphenylmethane diisocyanate, 2,4-diphenylmethane diisocyanate, and 1,5-naphthylene diisocyanate.

Mixtures of polyisocyanates can be used and also polyisocyanates which have been modified by the introduction of urethane, allophanate, urea, biuret, carbodiimide, uretonimine or isocyanurate residues.

Preferred polyisocyanates are 4,4'-dicyclohexylmethane diisocyanate, isophorone diisocyanate, toluene-2,4-diisocyanate, hexamethylenediisocyanate, 4,4'-diphenylmethane diisocyanate and 2,4-diphenylmethane diisocyanate.

It will be appreciated that the isocyanate-reactive component (a)(2) to (a)(4) may optionally include an isocyanate-reactive compound which is other than a polyol (e.g. a diamine or an aminoalcohol); however, the polyol component will normally be entirely or substantially comprised of polyol reactant.

Polyurethane A may be dispersible in water to form a stabilised dispersion solely by use of an external surfactant. Preferably polyurethane A has internal dispersing groups built into its structure (preferably in pendant and/or terminal positions) during its synthesis (usually as part of the prepolymer) which render the polyurethane self-water-dispersible, optionally in conjunction with an external surfactant. Such internal dispersing groups are more usually chain pendant groups and may be ionic (cationic or anionic) or nonionic, or a combination thereof, and may form part of the isocyanate-reactive components (a)(2) to (a)(4) and/or the polyisocyanate (a)(1), and/or may form part of the active hydrogen chain extending compound (b). Most preferably they form part of the isocyanate-reactive components (a)(2) to (a)(4) and/or the polyisocyanate (a)(1) since this results in a self-water-dispersible polyurethane prepolymer component.

Cationic dispersing groups comprised by the polyol (a)(2) and optionally (a)(4) are preferably quaternary ammonium groups, and examples of anionic dispersing groups are SO_3^- , -OSO_3^- , -PO_3^- , and in particular a carboxylate salt group -CO_2^- . Groups which are subsequently converted to dispersing groups are particularly unionised (or substantially unionised) acid or basic groups which can be converted to corresponding anionic or cationic groups by neutralisation or quaternisation. Where the dispersing groups are of the anionic type, such as carboxyl groups, which need to be in their neutralised form (such as carboxylate anionic groups) to effect their internal dispersing action, the required amount of dispersing groups could be achieved by neutralising only a certain proportion of the potential anionic groups (e.g. carboxyl groups) or alternatively, fully neutralising all such groups but having a lower amount of them in the polymer.

It is most preferred that ionic groups are incorporated into the prepolymer (and/or less preferably by being part of the chain-extender component) via unionised carboxylic-acid groups which are subsequently neutralised to carboxylate ion groups using agents such as a tertiary amine, examples of which include triethylamine, triethanolamine, dimethylethanolamine, dimethylaminoethylmethacrylate or N-methylmorpholine, or an alkaline hydroxide such as K, Na or Li hydroxide or a quaternary ammonium hydroxide.

Ammonia itself may also be used. Examples of reactants for effecting such incorporation include carboxyl group-bearing diols and triols, and in particular dihydroxy alkanolic acids. The most preferred carboxyl-bearing polyol is 2,2-dimethylol propionic acid (DMPA). Another preferred one is 2,2-dimethylol butanoic acid (DMBA). A mixture of DMPA and DMBA may also be used.

The conversion of any acid groups present in the prepolymer to anionic salt groups may be effected by neutralising the acid groups before, after or simultaneously with the formation of an aqueous dispersion of the prepolymer. Where acid groups are present additionally or only in the final polyurethane A by virtue of being incorporated additionally or only during the chain extension step the conversion of such groups to anionic salt groups may be effected by neutralising these acid groups before, during or after the formation of the final polyurethane A dispersion.

The acid value of the prepolymer is preferably between from 15 to 40 mg KOH/g prepolymer, more preferably between from 20 to 40 mg KOH/g prepolymer.

Nonionic dispersing groups comprised by polyol (a)(3) are typically pendant polyoxyalkylene groups, particularly polyethylene oxide (PEO) groups. Such groups may, for example be provided by employing as a reactant in the prepolymer formation (and/or less preferably by being part of the chain-extender component) diols having pendant PEO chains such as those described in the prior art, for example US 3905929. In US 3905929 examples of such compounds are disclosed which may be obtained by reacting one mole of an organic diisocyanate in which the two isocyanate groups have different reactivities with approximately one mole of a polyethylene glycol mono-ether and then reacting the adduct so obtained with approximately one mole of a dialkanolamine, for example diethanolamine. Chain-pendant PEO groups may also be introduced by employing certain amine and hydroxyl functional compounds, or diols, as disclosed in EP 0317258, where such compounds are obtained by oxyalkylating a defined polyether amine containing PEO residues.

If desired, the PEO chains may contain units of other alkylene oxides in addition to the ethylene oxide units. Thus, PEO chains in which up to 60% of the alkylene oxide units are propylene oxide units, the remainder being ethylene oxide units, may be used.

In the case of nonionic internal dispersing groups (such as PEO chains) it is preferred to use a composition as described above wherein polyurethane A has a polyethylene oxide content of less than 15% by weight, preferably less than 5% by weight by weight of ethylene oxide groups based on total polymer weight.

In a preferred embodiment the polyurethane A has a hard segment content (as described above) of $\geq 50\text{wt}\%$, more preferably $\geq 60\text{wt}\%$, especially preferably $\geq 70\text{wt}\%$ based on polyol molecular weight.

In a further preferred embodiment the polyols (a)(2) to (4) have a total ring structure content (as described above) of $\geq 45\text{wt}\%$, preferably $\geq 50\text{wt}\%$ based on polyol molecular weight.

The polymeric polyol of the isocyanate-reactive component (a)(4) is preferably a polymeric diol, but may be or include a polymeric polyol of functionality more than 2. This polymeric polyol preferably has a weight average molecular weight (hereinafter Mw) within the range of from 500 to 8,000 Daltons, more preferably from 700 to 3,000 Daltons. Such polyol is preferably essentially linear. Such polyol in principle may be selected from any of the chemical classes of polymeric polyols used or proposed to be used in polyurethane synthesis other than those described for components (a)(2) and (a)(3). In particular the polymeric polyol may be a polyester polyol, a polyesteramide polyol, a polyether polyol, a polythioether polyol, a polycarbonate polyol, a polyacetal polyol, a polyvinyl polyol and/or a polysiloxane polyol. An especially preferred polymeric polyol (a)(4) comprises a polycarbonate diol.

Polyester polyols which may be used include hydroxyl-terminated reaction products of polyhydric alcohols such as ethylene glycol, propylene glycol, diethylene glycol, neopentyl glycol, 1,4-butanediol, 1,6-hexanediol, furan dimethanol, cyclohexane dimethanol, glycerol, trimethylolpropane or pentaerythritol, or mixtures thereof, with polycarboxylic acids, especially dicarboxylic acids or their ester-forming derivatives, for example succinic, glutaric and adipic acids or their methyl esters, phthalic anhydrides or dimethyl terephthalate. Polyesters obtained by the polymerisation of lactones, for example caprolactone, in conjunction with a polyol may also be used. Polyesteramides may be obtained by the inclusion of amino-alcohols such as ethanolamine in polyesterification mixtures. Polyesters which incorporate carboxy groups may be used, for example polyesters synthesised by esterification of DMPA and/or DMBA with diols, provided that the esterification is carried out at temperatures below 200°C to retain the carboxy functionality in the final polyester.

Polyether polyols which may be used include products obtained by the polymerisation of a cyclic oxide, for example ethylene oxide, propylene oxide or tetrahydrofuran or by the addition of one or more such oxides to polyfunctional initiators, for example water, methylene glycol, ethylene glycol, propylene glycol, diethylene glycol, cyclohexane dimethanol, glycerol, trimethylolpropane, pentaerythritol or Bisphenol A. Especially useful polyether polyols include polyoxypropylene diols and triols, poly(oxyethylene-oxypropylene) diols and triols obtained by the simultaneous or sequential addition of ethylene and propylene oxides to appropriate initiators and polytetramethylene ether glycols obtained by the polymerisation of tetrahydrofuran.

The isocyanate-reactive component may also include one or more organic monools.

The active hydrogen-containing chain extending compound which may be reacted with the prepolymer component is preferably an amino-alcohol, a primary or secondary aliphatic, alicyclic, aromatic, araliphatic or heterocyclic diamine or polyamine (i.e. having 3 or more amine groups), or hydrazine or a substituted hydrazine, or a polyhydrazide (preferably a dihydrazide).

Water-soluble chain extenders are preferred.

Water itself may be used as an indirect chain-extender because it will slowly convert some of the terminal isocyanate groups of the prepolymer to amino groups (via unstable carbamic acid groups) and the modified prepolymer molecules will then undergo chain extension. However, this is very slow compared to chain extension using the above mentioned active hydrogen chain-extenders (which can be called added chain-extender compounds) which will provide the predominant chain extension reaction if used.

Examples of such added chain-extenders useful herein include ethylene diamine, diethylene triamine, triethylene tetramine, propylene diamine, butylene diamine, hexamethylene diamine, cyclohexylene diamine, piperazine, 2-methyl piperazine, phenylene diamine, toluylene diamine, xylylene diamine, tri(2-aminoethyl) amine, 3,3-dinitrobenzidine, 4,4'-diaminodiphenylmethane, methane diamine, m-xylene diamine, isophorone diamine, and adducts of diethylene triamine with acrylate or its hydrolysed products. Also materials such as hydrazine (e.g. in the form of its mono-hydrate), azines such as acetone azine, substituted hydrazines such as, for example, dimethyl hydrazine, 1,6-hexamethylene-bis-hydrazine, carbodihydrazine, dihydrazides of dicarboxylic acids and sulphonic acids such as adipic acid dihydrazide, oxalic acid dihydrazide, isophthalic acid dihydrazide, hydrazides made by reacting lactones with hydrazine such as gamma-hydroxybutyric hydrazide, bis-semi-carbazide, and bis-hydrazide carbonic esters of glycols. Another suitable class of chain-extenders is the so-called "Jeffamine" compounds with a functionality of 2 or 3 (available from Huntsman). These are polypropylene oxide (PPO) or PEO-based di or triamines, e.g. "Jeffamine" T403 and "Jeffamine" D-400.

Preferably the active hydrogen chain-extender component is or includes hydrazine (usually in the form of its monohydrate), or a di or triamine (usually a diamine) of molecular weight below 300.

When the chain-extender is an added component such as a polyamine or diamine or hydrazine, it may be added to the aqueous dispersion of prepolymer, be present in the aqueous medium when the prepolymer is dispersed therein, or be fed with the prepolymer to water.

There is further provided a composition according to the above wherein polyurethane A has a weight average molecular weight of between 50,000 and 1,000,000 Daltons, preferably between 80,000 to 700,000 Daltons, more preferably between 120,000 to 500,000 Daltons, as measured by Gel Permeation Chromatography (GPC), using THF as solvent and polystyrene standards.

The isocyanate-terminated polyurethane prepolymer may be prepared in conventional manner by reacting a stoichiometric excess of the organic polyisocyanate with the isocyanate-reactive component (and any other components) under substantially anhydrous conditions at a temperature between about 30°C and about 130°C until reaction between the isocyanate groups and the isocyanate-reactive (usually all hydroxyl) groups is substantially complete. During the production of the isocyanate-terminated

prepolymer the components are generally used in proportions corresponding to a ratio of isocyanate groups to isocyanate-reactive (usually all hydroxyl) groups from about 1.2:1 to 2.5:1, preferably from 1.4:1 to 2:1, more preferably from 1.6:1 to 2:1.

5 If desired, catalysts such as dibutyltin dilaurate or stannous octoate may be used to assist prepolymer formation. A diluent, such as an organic solvent or a reactive component, may optionally be added before, during or after prepolymer formation to control the viscosity provided it does not impede obtaining a solvent-free final dispersion (such solvent may thus subsequently need to be removed as far as is possible). Suitable solvents which may be used include acetone, methylethylketone, dimethylformamide, 10 diglyme, N-methylpyrrolidinone, ethyl acetate, ethylene and propylene glycol diacetates, alkyl ethers of ethylene and propylene glycol diacetates, alkyl ethers of ethylene and propylene glycol monoacetates, toluene, xylene and sterically hindered alcohols such as t-butanol and diacetone alcohol. The preferred solvents are water-miscible solvents such as N-methylpyrrolidinone, acetone and dialkyl ethers of glycol acetates or mixtures of 15 N-methylpyrrolidinone and methyl ethyl ketone. In cases where the vinyl polymer B is formed *in situ* with the polyurethane A, the solvent for use in the prepolymer (if having suitable solvent characteristics) may be or may comprise (e.g. optionally in conjunction with organic solvents of the type described above) a monomer which is subsequently polymerised as the or as part of the monomer system to form vinyl polymer B.

20 The polyurethane A is prepared as an aqueous dispersion by first dispersing an isocyanate-terminated polyurethane prepolymer (optionally carried in an organic solvent medium which may include or consist of an isocyanate-inert monomer for another polymer such as vinyl polymer B wherein the organic solvent can be easily removed) in an aqueous medium, followed by chain-extension of the prepolymer with an active hydrogen 25 compound. Dispersion of the prepolymer is preferably achieved utilising self-dispersibility properties of the prepolymer arising from internal dispersing groups, although free surfactant may additionally be employed if desired.

30 In an alternative embodiment, the prepolymer for polyurethane A may be dispersed in an aqueous medium in which vinyl polymer B is already present, followed by chain extension as described above. In a further alternative embodiment, known as mass dispersion, the prepolymer may be dispersed in an aqueous medium in which are already dispersed the monomer components for vinyl polymer B, followed by chain extension as described above. The monomer components for vinyl polymer B are then polymerised as described below. In yet a further embodiment, the manufacture of polymer A may be 35 carried out by a technique which comprises in-line mixing, as described in Research Disclosure(2002), 457(May), P772-P774.

The prepolymer may be dispersed in water using techniques well known in the art. Preferably, the prepolymer is added to the water with agitation or, alternatively, water may be stirred into the prepolymer component.

40 The chain extension can be conducted at elevated, reduced or ambient

temperatures. Convenient temperatures are from about 5°C to 90°C, more preferably from 10 to 60°C.

The total amount of chain-extender material employed (other than water) is preferably such that the ratio of active hydrogens in the chain-extender to NCO groups in the prepolymer component is preferably within the range of from 0.6:1 to 2.0:1 more preferably 0.8:1 to 1.2:1. Of course, when water is employed as an indirect chain-extender, these ratios will not be applicable since the water, functioning both as an indirect chain-extender and a dispersing medium, will be present in a gross excess relative to the residual NCO groups.

By a vinyl polymer herein is meant a homo- or copolymer derived from the addition polymerisation (using a free radical initiated process and usually in an aqueous medium), preferably by aqueous emulsion polymerisation, of a monomer composition comprising one or more monomers of the formula $\text{CH}_2=\text{CR}^1\text{R}^2$ where R^1 and R^2 are each independently selected from the group comprising H, optionally substituted alkyl of 1 to 20 carbon atoms (more preferably 1 to 8 carbon atoms), optionally substituted cycloalkyl of 5 to 20 carbon atoms, optionally substituted acyl and others. Such olefinically unsaturated monomers are referred to herein as vinyl monomers. Examples of such vinyl monomers include 1,3-butadiene, isoprene, styrene, α -methyl styrene, divinyl benzene, acrylonitrile, methacrylonitrile, vinyl halides such as vinyl chloride vinyl esters such as vinyl acetate, vinyl propionate, vinyl laurate, and vinyl esters of versatic acid such as VeoVaTM 9 and VeoVaTM 10 (VeoVa is a trademark of Shell), heterocyclic vinyl compounds, alkyl esters of mono-olefinically unsaturated dicarboxylic acids (such as di-n-butyl maleate and di-n-butyl fumarate, and olefinically unsaturated monocarboxylic or dicarboxylic acids, such as acrylic acid, methacrylic acid, 2-carboxyethyl acrylate, fumaric acid, maleic acid, and itaconic acid, and optionally substituted alkyl esters of 1 to 20 carbon atoms thereof such as methylmethacrylate, butylmethacrylate, dimethylaminomethacrylate, and dimethylaminopropylmethacrylate.

A particular feature of the invention is the hydrophobic nature of the vinyl polymer component B. Therefore, the vinyl monomers which form vinyl polymer B should themselves have to be hydrophobic. According to the present invention, vinyl polymer B comprises vinyl monomers comprising in total ≥ 70 wt% carbon, nitrogen and halogen based on vinyl monomer molecular weight, preferably ≥ 75 wt%, more preferably ≥ 80 wt%. Preferred hydrophobic vinyl monomers are 2-ethylhexylacrylate, styrene, acrylonitrile and trifluoroethylmethacrylate.

A further particular feature of the invention is the glass transition temperature (T_g) of the vinyl polymer B, which is the temperature at which it changes from a glassy brittle state to a plastic, rubbery state. Glass transition temperatures may be determined experimentally by Differential Scanning Calorimetry (DSC) or calculated theoretically by means of the Fox equation. In a further preferred embodiment of the present invention, the vinyl polymer B has a T_g of $\geq 30^\circ\text{C}$.

In another aspect of the invention, vinyl polymer B is multiphase, by which it is meant that it comprises at least two distinct Tg values. Preferably, vinyl polymer B has one phase of Tg <20°C (soft phase) and at least one phase of Tg >20°C (hard phase).

Vinyl polymer B preferably has a particle size distribution (psd) of from 25 to 600nm, and the psd may be monomodal or bimodal. In a preferred aspect of the invention, vinyl polymer B has a bimodal psd.

Vinyl polymer B may also be an oligomer-supported polymer, by which is meant a low molecular weight oligomer (typically 5,000 to 50,000 Daltons) is first prepared as a stabilising agent for the second phase of the polymer preparation of vinyl polymer B.

In a further embodiment, vinyl polymer B is present in the composition as a polymer hybrid (hereinafter a hybrid) by which is meant in this specification that the vinyl polymer B has been prepared in the presence of a polyurethane during and/or after the latter's formation. The hybrid may then be combined with further polymers, for example, the hybrid may be mixed with one or two separately prepared polymers, or with a sequentially formed pair of polymers (including oligomer supported polymers as described above).

Preferably the acid value of vinyl polymer B is ≤ 10 mg KOH/g polymer, more preferably ≤ 5 mg, especially zero.

The weight average molecular weight of polymer B is between 50,000 and 6,000,000 Daltons, preferably between 100,000 and 1,000,000 Daltons, more preferably between 500,000 and 1,000,000 Daltons.

Vinyl polymer B may often advantageously contain vinyl monomers which provide an adhesion and/or crosslinking functionality to the resulting polymer coating. Examples of these, some of which have already been mentioned above, include acrylic and methacrylic monomers having at least one free carboxyl, hydroxyl, epoxy, acetoacetoxy, or amino group, such as acrylic acid and methacrylic acid (and also their amides, hydroxyalkyl esters and amino alkyl esters), glycidyl acrylate, glycidyl methacrylate, aceto acetoxy ethyl methacrylate, t-butylamino ethyl methacrylate and dimethylamino ethyl methacrylate; other adhesion promoting monomers include heterocyclic vinyl compounds such as vinyl pyrrolidone and vinyl imidazole.

In one preferred embodiment of the invention, amino functionality can be incorporated into vinyl polymer B by preparing a polymer comprising vinyl monomer units of an olefinically unsaturated acid, such as acrylic acid or methacrylic acid and subsequently converting at least a proportion of the carboxylic acid groups to amino groups (as part of amino ester groups) by an imination reaction using an alkylene imine such as ethylene imine or propylene imine.

Vinyl polymer B may either be prepared separately and then admixed with polyurethane A or made *in situ*, i.e. in the presence of polyurethane A.

The polymerisation of the vinyl monomer composition to form vinyl polymer B will normally require the use of a free-radical-yielding initiator to initiate the polymerisation.

Suitable free-radical-yielding initiators include inorganic peroxides such as K, Na or hydrogen peroxide; persulphates such as ammonium persulphate or percarbonates; organic peroxides, such as acyl peroxides including for example benzoyl peroxide, alkyl hydroperoxides such as t-butyl hydroperoxide and cumene hydroperoxide; dialkyl peroxides such as di-t-butyl peroxide; peroxy esters such as t-butyl perbenzoate and the like; mixtures may also be used. The peroxy compounds are in some cases advantageously used in combination with suitable reducing agents (redox systems) such as Na or K pyrosulphite or bisulphite, and L-ascorbic acid. Azo compounds such as azoisobutyronitrile (AIBN) may also be used. Metal compounds such as Fe.EDTA (EDTA is ethylene diamine tetraacetic acid) may also be usefully employed as part of a redox initiator system. An initiator system partitioning between the aqueous and organic phases, for example a combination of t-butyl hydroperoxide, L-ascorbic acid and Fe.EDTA, may be of particular use. The amount of initiator or initiator system to use is conventional, for example within the range 0.05 to 6 wt % based on the total monomer used.

An aqueous polymerisation to pre-form vinyl polymer B normally needs to be performed in the presence of a stabilising and/or dispersing material, and when making an aqueous latex of a vinyl polymer, a conventional emulsifying agent would need to be employed (e.g. anionic and/or nonionic emulsifiers such as Na salts of dialkylsulphosuccinates, Na salts of sulphated oils, Na salts of alkyl sulphonic acids, Na, K and ammonium alkyl sulphates such as sodium lauryl sulphate, C₂₂₋₂₄ fatty alcohols, ethoxylated fatty acids and/or fatty amides, phosphate esters, alcoholvinylethoxylates, and Na salts of fatty acids such as Na stearate and Na oleate; the amount used is usually 0.1 to 5% by weight on the weight based on the total vinyl monomer used).

A buffer material, such as sodium bicarbonate, is often employed in polymerisations to form vinyl polymers.

If formed *in situ*, vinyl polymer B is made by an aqueous free-radical polymerisation process as described above, and such polymerisation may be performed simultaneously with the chain extension step of the prepolymer of polyurethane A, or performed subsequent to the chain extension step, or performed partly simultaneously with the chain extension step and partly subsequent to the chain extension step.

When making a hybrid, the monomer for making the *in situ* prepared polymer may be introduced in the process at any suitable stage. For example, when the aqueous dispersion of the urethane prepolymer is formed in the process to make the polyurethane polymer A, all of the vinyl monomer for the vinyl polymer B may be added to the prepolymer prior to its dispersion into water, or all of the vinyl monomer may be added subsequent to dispersion (or may have already been added to the water prior to the dispersion of the prepolymer therein), or part of the vinyl monomer may be added to the prepolymer prior to dispersion and the remainder added subsequent to dispersion. In the case where all or part of the vinyl monomer is added to the prepolymer prior to dispersion

into water, such vinyl monomer could be added to the prepolymer subsequent to its formation or prior to its formation, or some could be added subsequent to its formation and some added prior to its formation. In the case where any vinyl monomer is added prior to the prepolymer formation it may provide at least part of a solvent system for the reaction to form the prepolymer. Particular examples of such processes are detailed in patents US5137961 and US4664430 which are herein incorporated by reference.

When using an *in situ* process however to form vinyl polymer B, a polyurethane polymer containing internal dispersing groups such as polyurethane A usually removes the requirement for the use of a separately added conventional emulsifying agent since the polyurethane itself acts as an effective dispersant for the polymerisation, although a conventional emulsifier can be still employed if desired.

A further aspect of the invention comprises a composition as hereinbefore described wherein either or both of polyurethane A or vinyl polymer B are present at least as part of a hybrid.

In the invention dispersion, it is preferred that the weight average particle diameter (D_w) (i.e. the particle size - since the particles are essentially spherical) of the polyurethane A particles is within the range of from 20 to 400 nm, more preferably 30 to 150 nm. The D_w of the vinyl polymer B particles is preferably within the range of from 30 to 500 nm, more preferably from 45 to 250 nm and most preferably from 60 to 200 nm. (It is to be understood that D_w is also applicable to, i.e. is the average of, bimodal or polymodal particle size distributions, as well as monomodal distributions).

The solids content of an aqueous composition of the invention is usually within the range of from about 20 to 65 wt % on a total weight basis, more usually 30 to 55 wt %. Solids content can, if desired, be adjusted by adding water or removing water (e.g. by distillation or ultrafiltration).

A yet further aspect of the present invention is a composition as hereinbefore described which further comprises functionality capable of crosslinking. Such crosslinking functionality may be present on either or both of polyurethane A or vinyl polymer B and may either give rise to crosslinking without the need for added external crosslinker (*in situ* crosslinking, or "pre-crosslinking") and/or may give rise to crosslinking only upon addition of an external crosslinker to the aqueous composition of the invention.

When polyurethane A comprises functionality which imparts *in situ* cross linking, this is preferably from one or more of the components which are used to form the isocyanate-terminated prepolymer described above. Preferably such functionality is present on at least one of the polyols (4) above.

When vinyl polymer B comprises functionality which imparts *in situ* crosslinking this is preferably from one or more of the vinyl monomers which are used to form vinyl polymer B; preferably the functionality capable of crosslinking is selected from amino, carbonyl, carboxy, hydroxy, and olefinic functionalities. Further preferably, the functionality capable of crosslinking comprises olefinically unsaturated bond functionality. Examples of

preferred vinyl monomers include allyl methacrylate, tetraethylene glycol methacrylate, and divinyl benzene. Such vinyl monomers are normally used in an amount of from 0.1 to 10 weight %, more usually from 0.1 to 5 weight % of the total weight of vinyl monomers used for the polymerisation of vinyl polymer B.

5 In a particular embodiment of the present invention composition, there is described a composition wherein the olefinically unsaturated bond functionality capable of crosslinking is susceptible to initiation by radiation to form a covalent bond. It is especially preferred that this radiation is uv radiation. Radiation initiated crosslinking may be carried out with or without added photoinitiator. In a preferred embodiment, the composition of the
10 present composition also comprises one or more multifunctional materials (hereinafter MFAs) which carry two or more radiation polymerisable ethylenically unsaturated bonds which are capable of crosslinking with the olefinically unsaturated bond functionality present on the composition of the present invention.

A wide variety of MFAs may be employed. Typical examples include :

- 15 1. Epoxy (meth)acrylates;
2. Urethane (meth)acrylates;
3. Multi-functional (meth)acrylate monomers; and
4. Amine-(meth)acrylate adducts.

Epoxy (meth)acrylates are those products formed by the reaction of (meth)acrylic acid
20 with an epoxy(glycidyl) functional component e.g. aliphatic and aromatic containing epoxy resins, epoxidised oils, acrylic polymers and acrylic grafted polymers in which the acrylic component contains pendent epoxy groups. Some of the (meth)acrylic acid may be replaced by other acids, both ethylenically unsaturated and saturated, so as to impart specific properties e.g. aliphatic acids, fatty acids and aromatic acids. These products may
25 alternatively be prepared by the reaction of a carboxylic acid functional component (e.g. polyesters and acrylic polymers) with a second component containing both epoxy groups and ethylenic unsaturation e.g. glycidyl (meth)acrylate.

Urethane (meth)acrylates are those products formed by the reaction of an isocyanate containing component with a hydroxyl containing component. At least one of these
30 components must contain ethylenic unsaturation. Examples of isocyanate functional components are hexamethylene diisocyanate, isophorone diisocyanate, isocyanate functional acrylic polymers and polyurethanes, reaction products of hydroxyl functional components (e.g. poly-ethylene glycol, poly-propylene glycol and di-, tri- and etc-hydroxy aliphatic alcohols (e.g. glycerol and trimethylolpropane) and their ethoxylated,
35 propoxylated and polycaprolactone analogs) with di-, tri- and etc-isocyanates (e.g. hexamethylene diisocyanate, isophorone diisocyanate and TDI). Examples of hydroxy containing ethylenically unsaturated components are hydroxyethyl (meth)acrylate and its ethoxylated, propoxylated and polycaprolactone analogs.

Multi-functional (meth)acrylate monomers are (meth)acrylic acid esters of di-, tri- and etc-
40 hydroxyl alcohols (e.g. poly-ethylene glycol, poly-propylene glycol, aliphatic diols,

neopentyl glycol, ethoxylated bisphenol A, trimethylolpropane, pentaerythritol, glycerol, di-trimethylolpropane, hydroxyl functional polyesters, dipentaerythritol and the ethoxylated, propoxylated and polycaprolactone analogues of all the above.

Amine-(meth)acrylate adducts are those products prepared by the partial "Michael Type Addition" of primary and secondary amines to ethylenic unsaturation i.e. the double bond of (meth)acrylate containing compounds. Of particular interest here are the multi-functional (meth)acrylate monomers as mentioned above. Examples of amine-acrylate adducts are diethylamine modified trimethylolpropane triacrylate and ethanolamine modified ethoxylated trimethylolpropane triacrylate.

All of the above listed acrylates and methacrylates may incorporate specific hydrophilic components to facilitate their being dissolved, emulsified or dispersed in an aqueous phase. Examples are the addition of secondary amines, phosphoric acid and anhydrides (e.g. succinic anhydride, phthalic anhydride and tetrahydrophthalic anhydride). The resulting tertiary amines and pendent carboxylic acid groups are then neutralised. Another hydrophilic group of particular interest is poly-ethylene glycol.

Preferably such materials are substituted and unsubstituted (meth)acrylates. Preferred examples are the esters of (meth)acrylic acid with monohydric and polyhydric compounds such as ethyl, butyl, hexyl, octyl, and decyl (meth)acrylates; neopentyl (meth)acrylate, trimethylolpropane tri(meth)acrylate (TMPTA), pentaerythritol tri(meth)acrylate and tetra(meth)acrylate, caprolactone (meth)acrylates, alkoxylated (meth)acrylates, glycerol (meth)acrylates, 1,4-butanediol di(meth)acrylate, 2,2-dimethyl-3-hydroxypropyl-2,2-dimethyl-3-hydroxypropionate di(meth)acrylate, isobornyl (meth)acrylate, tripropylene glycol di(meth)acrylate, urethane (meth)acrylates, (meth)acrylated epoxides and the like. Especially suitable are (meth)acrylates such as TMPTA which have a hydrophobic character. In this respect, it is preferred that the total amount of ethylene oxide present in the MFA is <80wt% based on the molecular weight of the MFA, more preferably <50 wt%, most preferably < 35 wt%.

Such MFAs are preferably present at a level of from 1 to 30wt% based on total polymer weight, more preferably from 2 to 20 wt% especially from 5 to 15 wt%.

In a yet further embodiment of the present invention, there is provided a composition as hereinbefore described which further comprises $\leq 5\text{wt}\%$ of an external crosslinker based on total polymer weight (A+B), more preferably $\leq 3 \text{ wt}\%$, especially preferably $\leq 2 \text{ wt}\%$.

The crosslinker is preferably selected from but not limited to the group comprising the following types: urea-formaldehyde, melamine-formaldehyde, carbodiimide, aziridine, epoxy, silanes and/or mixtures thereof. It is preferred that the crosslinking takes place at or around ambient temperature, and does not require excess application of heat e.g. stoving.

There is further provided according to the invention an aqueous coating composition as defined above which is substantially solvent-free. By a substantially

solvent-free aqueous composition, is meant that the composition must contain less than 1.5 wt % of organic solvent based on total polymer solids, more preferably less than 0.5 wt %, and most preferably no solvent at all. It is particularly preferred that the aqueous composition contains less than 5 wt % of organic solvent based on polyurethane A solids, more preferably less 2 wt %, and most preferably no solvent at all. (In this specification organic plasticisers are intended to be within the scope of the term "solvent"; these, like coalescent solvents, are also used in the art to decrease minimum film forming temperature (MFFT) although strictly speaking they are not solvents). In a particularly preferred embodiment of the present invention, the composition as herein described is totally solvent (and therefore plasticiser) free.

In an embodiment of the present invention there is provided a process for the manufacture of a composition as herein described which comprises the following steps:

- (I) (i) reaction of components (a)(1) to (a)(4) together to form an isocyanate-terminated prepolymer;
- (ii) dispersion of the isocyanate-terminated prepolymer in water;
- (iii) chain extension of the isocyanate-terminated prepolymer by reaction with an active-hydrogen chain extending compound to form polyurethane A; and
- (II) admixture of preformed vinyl polymer B.

In a further embodiment of the invention there is provided a process for the manufacture of a composition as herein described which comprises the following steps:

- (I) (i) reaction of components (a)(1) to (a)(4) together to form an isocyanate-terminated prepolymer;
- (ii) dispersion of the isocyanate-terminated prepolymer in water;
- (iii) chain extension of the isocyanate-terminated prepolymer by reaction with a active-hydrogen chain extending compound to form polyurethane A;
- (II) admixture of vinyl monomer followed by reaction under conditions sufficient to effect polymerisation to form vinyl polymer B.

In both of the above embodiments, steps (ii) and (iii) may be performed in any order, and step (II) can occur at any stage in the process.

When the invention comprises a hybrid, it is preferred that the weight ratio of the polyurethane A to the other polymer in the hybrid is within the range of from 5:95 to 99:1 more preferably from 15:85 to 90:10, and most preferably from 30:70 to 80:20.

Any or all of the above described processes for the manufacture of polymers A or B may be carried out by a technique which comprises in-line mixing, or the technique of mass dispersion, as described above.

The composition of the current invention may for example be used, appropriately formulated if necessary, for the provision of films, including *inter alia* polishes, varnishes, lacquers, or paints. The composition of the current invention may also be used for the provision of inks or adhesives. Optional further additives or components (to form compositions) include *inter alia* defoamers, rheology control agents, thickeners, dispersing

and stabilising agents (usually surfactants), wetting agents, fillers, extenders, fungicides, bacteriocides, anti-freeze agents, waxes and pigments.

In a particularly preferred embodiment, the composition as described herein further comprises a pigment and/or an extender. Incorporation of pigment into currently known polymer dispersions often has a deleterious effect on stain resistance properties. A particular advantage of compositions of the current invention is that the stain resistance of the unpigmented, or 'clear', composition is maintained in the corresponding pigmented composition. Pigments which may be used in the present invention include, for example, titanium dioxide, iron oxide, chromium-based compounds and metal phthalocyanine compounds. They are finely divided inorganic or organic powders (usually of particle size in the region of 0.1 to 10 μ m, and obtained e.g. by grinding or milling) for achieving properties such as colour, opacity, and hiding power. They are usually incorporated into a coating composition in the form of a dry powder or a uniform dispersion of the pigment in a suitable carrier medium. Titanium dioxide (a white pigment) is the most preferred pigment in the present invention. Extenders which may be used include calcium carbonate and china clay.

There is further provided a composition as described herein with a pigment volume concentration (PVC) of from 10 to 35%, preferably 10 to 30%, more preferably 15 to 25%, wherein PVC is defined as:

$$\frac{[volume\ (pigment) + volume\ (extender)]}{[volume\ (pigment) + volume\ (extender) + volume\ (binder)]}$$

wherein "binder" refers to the polymer composition according to the first embodiment of the present invention.

The compositions once applied may be allowed to dry naturally at ambient temperature, or the drying process may be accelerated by heat, in order to give a film.

A particular advantage of compositions according to the present invention when in the form of a film is the resistance of the film to staining. An important property of these films in determining the stain resistance is the moisture vapour transmission rate (MVTR), which is a measure of the barrier properties of the film, in particular to water. A high value of MVTR indicates a film with high breathability and low barrier properties, whereas a low value of MVTR indicates a film with high barrier properties. For the purposes of the present invention, lower values of MVTR are preferred. Under the conditions for measurement of MVTR described below, films according to the present invention have an MVTR of $\leq 500\text{ g/m}^2/24\text{h}$, preferably $\leq 475\text{ g/m}^2/24\text{h}$, more preferably $\leq 450\text{ g/m}^2/24\text{h}$.

Preferred substances to which films of the present invention demonstrate stain resistance are those referred to in standard test method DIN 68861(Pt 1B), namely: acetone, ethylbutylacetate, sodium carbonate, ammonia, petrol, disinfectant, acetic acid, citric acid, ethyl alcohol, detergent, red wine, beer, mustard, salt, onion, cola, coffee, tea, blackcurrant juice, evaporated milk, water, butter, olive oil, lipstick, black rollerball, printing

ink, ethanol, handcream and 'Andy' cleaner (a common Dutch detergent). It is particularly preferred that aqueous coating compositions, as hereinbefore described according to the present invention, when in the form of a film exhibit a total stain resistance value to coffee, ethanol, mustard and red wine of ≥ 30 , more preferably of ≥ 35 .

5 There is further provided according to the invention a method of coating the surfaces of a substrate using an aqueous composition as defined above. Preferably the substrate comprises architectural surfaces. Preferably such surfaces are porous, more preferably the surfaces are wood. In particular the compositions of the present invention are useful and suitable for providing the basis of protective coatings for wooden
10 substrates (e.g. wooden floors, furniture and window frames), plastics and paper.

 There is further provided according to the invention a coating obtained from a composition or a film or by a method as described above.

 There is further provided according to the invention a substrate having a coating obtained as described above.

15 There is also provided a film obtained from a composition as described above.

 The present invention is now further illustrated but in no way limited by reference to the following examples. Unless otherwise specified all parts, percentages, and ratios are on a weight basis.

20 Examples

Example 1 (E1)

25 Polycarbonate-diol containing aliphatic urethane-acrylic hybrid was prepared using the components listed below in Table 1. The acid value of the polyurethane component is 21.6 mg KOH/g polyurethane polymer. The total wt% of ring structures in the diol components comprised by the urethane component is 64%, the total wt% of hard segment content of the urethane is 78%, the total wt% carbon and halogen on molecular weight of the vinyl monomer mixture is 90% and the Tg of the vinyl component is 30°C. The ratio of
30 urethane:acrylic in E1 is 40:60 based on polymer weight.

Table 1

Component	No.	solids (%)	Weight used (g)
NeoRez™ R-986	1	35.0	750.00
demineralised water	2	0.0	653.90
t-butylhydroperoxide	3	70.0	1.74
demineralised water	4	0.0	10.46
FeEDTA	5	1.0	1.74
i-ascorbic acid	6	100.0	0.69
demineralised water	7	0.0	67.72
ammonia	8	0.0	0.50
2-ethylhexylacrylate (I)	9	100.0	66.94
styrene (I)	10	100.0	129.94
2-ethylhexylacrylate (II)	11	100.0	66.94
styrene (II)	12	100.0	129.94
Total Weight			1880.51
Total solids			35.0

A 2 litre 3-necked round bottom flask, equipped with a stirrer and a thermometer,
 was charged with components (1) and (2). Subsequently, the first (I) phase monomer
 mixture (components (9) and (10)) was added to the reaction mixture under a nitrogen
 atmosphere. The mixture was stirred for 60 minutes at 25°C, and a slurry of components
 (3) and (4) was then added followed by component (5). To initiate polymerisation of the
 first phase monomer mixture, 25 wt% of the iso-ascorbic acid solution ((6), (7) and (8),
 pH>8) was added. The reaction was exothermic and reached a peak temperature, fifteen
 minutes after which, the second (II) phase monomer mixture (components (11) and (12))
 was added and again allowed to mix for 60 minutes. A further 25 wt% of the initiator
 solution of components (6), (7) and (8) was then added. The reaction again exhibited an
 exotherm and fifteen minutes after peak temperature a post-reaction was carried out in
 order to polymerise residual small levels of free monomer, which comprised addition of
 the remainder (50 wt%) of the initiator solution of components (6), (7) and (8) over a
 period of 30 minutes. The batch was filtered through a filter cloth to remove any coagulum
 formed during the reaction.

Comparative Example 1 (CE1)

Comparative example 1 is NeoPac™ E-110, a proprietary product of NeoResins
 bv, which is a self cross linking urethane-acrylic hybrid. The acid value of the polyurethane
 component is 28.6 mg KOH/g polyurethane polymer. The solids content of dispersion CE1
 is 35% and the pH is approximately 8. The total wt% of ring structures in the diol

components comprised by the urethane component is 40%, the wt% of hard segment content of the urethane part is 75%. The Tg of the vinyl component is 21°C and the total wt% of carbon and halogen on molecular weight of the vinyl monomer mixture is 67%. The ratio of urethane:acrylic in CE1 is 50:50 based on polymer weight.

Comparative Example 2 (CE2)

Comparative example 2 is NeoPac™ E-121, a proprietary product of NeoResins bv, which is a dimer fatty acid containing urethane-acrylic hybrid. The acid value of the polyurethane component is 14.3 mg KOH/g polyurethane polymer. The solids content of dispersion E1 is 35% and the pH is approximately 8. The total wt% of ring structures in the diol components comprised by the urethane component is 37%, the wt% of hard segment content of the urethane part is 65%. The Tg of the vinyl component is 28°C and the total wt% of carbon and halogen on molecular weight of the vinyl monomer mixture is 64%. The ratio of urethane:acrylic in CE2 is 50:50 based on polymer weight.

Testing methods

1. Moisture Vapour Transmission Rate (MVTR)

All MVTR testing for films derived from compositions according to the present invention was carried out under what are normally referred to as "tropical" conditions and with wet film thickness of 12 micron.

Clear Formulation

The following formulation was used for all examples (E1, CE1, CE2) to determine MVTR values. All amounts are parts by weight.

<u>No.</u>	<u>Ingredient:</u>	<u>Amount:</u>	<u>Type of material:</u>	<u>Supplier:</u>
1	Example dispersion	87.50	Binder	NeoResins bv
2	Dowanol™ DPnB	8.75	Coalescent	Dow Chemical
3	Demineralised water	3.75		
	Total=	100.00		

Ingredients No.s 2 and 3 were added to (1) with stirring. The formulated samples were allowed to equilibrate for at least 24 hours at room temperature prior to testing.

MVTR test conditions (ASTM D1653-91a)

The formulated sample was applied (12 micron wet film thickness) onto china clay coated paper board (400 g/m², available from HCG Grafigroep, Netherlands) and allowed to dry at room temperature for 1 hour. Subsequently, the films were aged in an oven at 50°C for 16 hours. After ageing, the films were allowed to cool down to room temperature for at least 1 hour.

For each coated paper board at least three dishes were prepared for MVTR assessment. Each dish was first filled with desiccant (anhydrous calcium chloride) to within 6 mm of the top edge, and a thin layer of paraffin wax was smeared around the ring of each dish. Using a circular cutting knife the three samples of paper board were cut and each one was placed (coated side up) over a rim of a dish. A metal ring was placed on the dish and the initial weight of the dish was measured. The dish was secured with two elastic bands and placed in a humidity cabinet, which was maintained at a constant temperature and relative humidity (R.H.) of 38°C and 90% R.H. (i.e. tropical conditions). The dishes were weighed after 1 and 4 days (without elastic bands) and the MVTR value was calculated using the three formulae below:

$$MVTR(1) = \frac{(1 \text{ day weight (g)} - \text{initial weight (g)}) \times 24h}{\text{time (h)} \times \text{area substrate (m}^2\text{)}}$$

$$MVTR(4) = \frac{(4 \text{ day weight (g)} - 1 \text{ day weight (g)}) \times 24h}{\text{time (h)} \times \text{area substrate (m}^2\text{)}}$$

$$MVTR (\text{average}) = \frac{MVTR(1) + MVTR(4)}{2}$$

All values reported below in Table 2 are MVTR (average) values in units of g/m²/24h. The exposed substrate area was in all cases 5 x 10⁻³m².

Table 2

Formulated Example	MVTR (average) (g/m ² /24h)
E1	463
CE1	563
CE2	585

2. Stain Resistance assessment

2.1 Clear formulation

The following clear formulation was used for all examples (E1, CE1, CE2) to determine the level of stain resistance of the final coated material. All amounts are parts by weight.

No.	Ingredient:	Amount:	Type of material:	Supplier:
1	Example dispersion	85.18	binder	NeoResins bv
2	Dowanol™ DPM	7.10	coalescent	Dow Chemical
3	Dowanol™ DPnB	1.42	coalescent	Dow Chemical
5 4	Byk™ 346	0.34	wetting agent	Byk Chemie
5	TS-100	0.85	matting agent	Degussa
6	Aquacer™ 513	3.83	wax	Byk Cera
7	Byk™ 024	0.68	defoamer	Byk Chemie
8	BR-125/water (1/1)	0.60	thickening agent	
10	Total= 100.00			

Ingredients (2) and (3) were premixed and added to (1) while stirring. Subsequently ingredients (4 – 8) were added with stirring in respective order. The formulated samples were left to equilibrate for at least 24 hours at room temperature.

2.2 Pigmented formulation

The following pigmented formulation was used for all examples (E1, CE1, CE2) to determine the level of stain resistance of the final coated material. All amounts are parts by weight.

No.	Ingredient:	Amount:	Type of material:	Supplier:
1	Example dispersion	62.17	binder	NeoResins bv.
2	Dowanol™ DPM	5.18	coalescent	Dow Chemical
3	Dowanol™ DPnB	1.04	coalescent	Dow Chemical
25 4	Byk™ 346	0.25	wetting agent	Byk Chemie
5	TS-100	0.62	matting agent	Degussa
6	Aquacer™ 513	2.80	wax	Byk Cera
7	Byk™ 024	0.50	defoamer	Byk Chemie
8	BR-125 / demi water (1/1)	0.44	thickener agent	
30 9	Propylene glycol	1.88	coalescent	BASF/Lyondell
10	Demineralised water	4.17	n.a.	n.a.
11	AMP-95	0.21	neutralizing agent	Agnus Chemie
12	Dehydran™ 1293	0.42	defoamer	Cognis
13	Disperse Ayd™ W-22	0.31	wetting agent	Elementis
35 14	NeoCryl™ BT-24	1.56	pigment dispersant	NeoResins bv.
15	Tioxide™ TR-92	18.45	pigment	Huntsman
Total= 100.00				

Ingredients (2) and (3) were premixed and added to (1) while stirring. Subsequently ingredients (4 – 8) were added in respective order. Ingredients (9 – 15)

were premixed in respective order to prepare the pigment paste. Finally, this premix was added and the formulation was mixed at high speed. The formulated samples were left to equilibrate for at least 24 hours at room temperature.

5 Stain Resistance (DIN 68.861, Pt 1B)

The formulated examples prepared as described above (either clear or pigmented) were cast onto a Leneta test chart using a wire rod at a wet film thickness of 100 micron. The cast films were then allowed to dry at room temperature for 1 hour, followed by ageing of the coatings at 50°C for 16 hours. The coatings were allowed to cool to room temperature for 1 hour.

The stain resistance of the coated cards towards the following stains were then assessed: coffee, ethanol (48%), mustard and red wine. In all four cases, a spot (1cm²) of the respective stain was placed on the coating and covered with a piece of filter paper and a watch glass. In the case of coffee and ethanol (48%) resistance assessment, the spot was left for 16 hours, whereas for mustard and red wine it was left for 5 hours. After these periods, the spot was gently wiped off with a tissue and the film was assessed for its integrity. This was rated between 0 to 10, where 0 = film totally destroyed/strongly discoloured and 10 = film fully intact without any defects/discolouration. The total value of the four respective stain resistances was then calculated, where the theoretical maximum value would be 40. The results are shown in Table 3 and Table 4.

Table 3 (clear coatings)

STAIN	E1	CE1	CE2
Coffee	10	8	8
Ethanol	7	7	7
Mustard	10	5	2
Red wine	10	5	4
Total	37	25	21

Table 4 (pigmented coatings)

STAIN	E1	CE1	CE2
Coffee	9	5	5
Ethanol	9	9	9
Mustard	9	5	2
Red wine	10	4	3
Total	37	23	19

Claims

1. An aqueous coating composition comprising:

- (i) 20 to 80 wt% of a polyurethane A which has an acid value of 8 to 40 mg KOH/g polyurethane A and a hard segment content of ≥ 40 wt% by weight of polyurethane A; and
(ii) 20 to 80 wt% of a vinyl polymer B which has a glass transition temperature of $\geq 20^{\circ}\text{C}$;

wherein (i) and (ii) add up to 100 %;

which when in the form of a film exhibits a moisture vapour transmission rate of $\leq 500\text{g/m}^2/24\text{h}$.

2. A composition according to claim 1 wherein polyurethane A is obtained by the reaction of:

(a) an isocyanate-terminated prepolymer formed from components which comprise:

- (1) 20 to 80 wt% of at least one polyisocyanate;
(2) 3 to 10 wt% of at least one polyol of weight average molecular weight less than 500 Daltons, containing at least one ionic or potentially ionic water-dispersing group, and having two or more isocyanate-reactive groups;
(3) 0 to 15 wt% of at least one polyol containing non-ionic water dispersing groups having two or more isocyanate-reactive groups;
(4) 30 to 80 wt% of at least one polyol other than (2) or (3), having two or more isocyanate-reactive groups;

where (1), (2), (3), and (4) add up to 100%; and

(b) an active-hydrogen chain extending compound.

3. An aqueous coating composition according to claim 2 wherein the polyols (a)(2) to (4) have a total ring structure content of $\geq 45\text{wt}\%$.

4. An aqueous coating composition according to claim 3 wherein the polymeric polyol (a)(4) comprises a polycarbonate diol.

5. A composition according to any one of the preceding claims wherein polyurethane A has a weight average molecular weight of between 50,000 and 1,000,000 Daltons.

6. An aqueous coating composition according to any one of the preceding claims wherein vinyl polymer B comprises vinyl monomers comprising in total ≥ 70 wt% carbon, nitrogen and halogen based on vinyl monomer molecular weight.

7. An aqueous coating composition according to claim 6 wherein the vinyl monomer is selected from the group consisting of 2-ethylhexylacrylate, styrene, acrylonitrile and

trifluoroethylmethacrylate.

- 5 8. An aqueous coating composition according to any one of the preceding claims wherein the acid value of polymer B is ≤ 10 mg KOH/g polymer.
9. A composition according to any one of the preceding claims wherein vinyl polymer B comprises a multiphase polymer.
- 10 10. A composition according to any one of the preceding claims wherein vinyl polymer B has a weight average molecular weight of between 50,000 and 1,000,000 Daltons.
11. A composition according to any of the preceding claims wherein either or both of polyurethane A or vinyl polymer B are present at least as part of a hybrid.
- 15 12. An aqueous coating composition according to any one of the preceding claims wherein polyurethane A and/or vinyl polymer B further comprises functionality capable of crosslinking.
- 20 13. An aqueous coating composition according to any one of the preceding claims further comprises ≤ 5 wt% of an external crosslinker based on total polymer weight (A+B).
- 25 14. An aqueous coating composition according to any one of the preceding claims which when in the form of a film exhibits a total stain resistance value to coffee, ethanol, mustard and red wine of ≥ 30 .
15. A composition according to any one of the preceding claims which further comprises a pigment.
- 30 16. A composition according to claim 15 with a pigment volume concentration of from 10 to 35%.
17. A composition according to any one of the preceding claims which is substantially solvent free.
- 35 18. A process for the manufacture of a composition according to any one of claims 1 to 17 which comprises the following steps:
- (I) (i) reaction of components (a)(1) to (a)(4) together to form an isocyanate-terminated prepolymer;
- (ii) dispersion of the isocyanate-terminated prepolymer in water;
- 40 (iii) chain extension of the isocyanate-terminated prepolymer by reaction with an

- (II) active-hydrogen chain extending compound to form polyurethane A; and
admixture of preformed vinyl polymer B.

19. A process for the manufacture of a composition according to any one of claims 1 to 17 which comprises the following steps:

(I) (i) reaction of components (a)(1) to (a)(4) to form an isocyanate-terminated prepolymer;

(ii) dispersion of the isocyanate-terminated prepolymer in water;

(iii) chain extension of the isocyanate-terminated prepolymer by reaction with an active-hydrogen chain extending compound to form polyurethane A;

(II) admixture of monomer followed by reaction under conditions sufficient to effect emulsion polymerisation to form vinyl polymer B.

20. A film obtained from a composition according to any one of claims 1 to 17.

21. A method of coating the surfaces of a substrate using an aqueous composition according to any one of claims 1 to 17.

22. A method according to claim 21 wherein the surfaces are porous.

23. A method according to claim 22 wherein the surfaces are wood.

24. A coating obtained from a composition according to any of claims 1 to 17.

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